

## PATENT COOPERATION TREATY



PCT

REC'D 20 SEP 2006

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY PCT

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference IN/PA-271	<b>FOR FURTHER ACTION</b>		See Form PCT/IPEA/416
International application No. PCT/IN2005/000042	International filing date (day/month/year) 10.02.2005	Priority date (day/month/year) 11.02.2004	
International Patent Classification (IPC) or national classification and IPC INV. C21C7/00			
Applicant TATA STEEL LIMITED et al.			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of 13 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input checked="" type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> <i>(sent to the International Bureau only)</i> a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand  15.09.2005		Date of completion of this report  19.09.2006	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer  Boureau, Jean-Louis  Telephone No. +49 89 2399-8454 	

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/IN2005/000042

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**Box No. I Basis of the report**

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1. With regard to the **language**, this report is based on

- ☒ the international application in the language in which it was filed
- ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
  - ☐ international search (under Rules 12.3(a) and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4(a))
  - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))

2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

**Description, Pages**

1-11 filed with the demand

**Claims, Numbers**

1-9 filed with the demand

**Drawings, Sheets**

1/3-3/3 as published

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

4. ☒ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

- ☒ the description, pages 6
- ☒ the claims, Nos. 4,5
- ☐ the drawings, sheets/figs
- ☐ the sequence listing (*specify*):
- ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	2-5, 9
	No: Claims	1,6-8
Inventive step (IS)	Yes: Claims	
	No: Claims	1-9
Industrial applicability (IA)	Yes: Claims	1-9
	No: Claims	

2. Citations and explanations (Rule 70.7):

**see separate sheet**

**Re Item I**

**Basis of the report**

The amendments filed with the letter dated 15.09.2005, i.e. with the Demand for International Preliminary Examination, introduce subject-matter which extends beyond the content of the application as filed, contrary to Article 34(2)(b) PCT. The amendments concerned are the following: description, page 6, last line and claims 4 and 5. In the application as originally filed, there cannot be found any basis for the ranges of injection speed of 110-120 m/mn, 60-80 m/mn and 100-120 m/mn.

Said amendments are not considered in the following reasoned statement.

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

Reference is made to the following documents:

- D1: US 2001/10181 A
- D2: US 4892580 A
- D3: EP 0123632 A
- D4: US 4094666 A

Document D1 discloses a cored wire injection process having the features of the preamble of claim 1. The wire is fed at a controlled velocity so as to penetrate into the molten steel at a predetermined speed and direction, especially at a depth that is substantially below the top surface of the molten steel (D1, paragraph [0020] and last sentence of paragraph [0013]). The purpose is to reduce time consumption and waste of energy and to promote more efficient mixing of the flux with the molten steel.

Due to the relative meaning of the word "close", no clear difference may be seen between (i) the requirement of claim 1 that the additives are released close to the bottom and (ii) the embodiment of document D1, Fig. 3, especially in conjunction with the last sentence of paragraph [0013].

In claim 1, the features "cored wire of appropriate dimensions, depending on the grade of liquid steel, treatment temperature and ladle size/liquid column height" are so vague that they do not make any difference with the process known from D1.

Therefore, the subject-matter of claim 1 is lacking of novelty with regard to D1 (Article 33(1) PCT). The same applies to dependent claim 7 (see D1, paragraph [0022]).

For similar reasons the process of claim 1 is lacking of novelty with regard to D4 (see especially claim 1, column 4, lines 5 to 17, Fig. 1).

The additional features of dependent claims 2 to 5 are either known or obviously derivable from D2, column 2, lines 6 to 11, column 3, lines 6 to 10, Examples 1 and 2.

Document D3 discloses a cored wire injection process for introducing calcium in molten steel. The features of dependent claims 7 and 8 are disclosed by D3, page 3, lines 8 to 10.

Document D4, claim 5, discloses the additional features of claims 6 to 8.

The use of calcium iron as calcium bearing material in a process for treating molten steel is conventional (see also the description of the application, page 2, lines 3, 4 and page 11, line 3). Therefore, the subject-matter of claim 9 does not appear to involve an inventive step (Article 33(2) PCT).

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**A CORED WIRE INJECTION PROCESS IN STEEL MELTS****FIELD OF INVENTION**

The present invention relates to a cored wire injection process in steel melts. In particular, it relates to the dimension and the injection speed of a cored wire used in steel plants to inject fluxes and alloying additives in molten steel baths.

The objectives of such additions are either to refine the steel further or to adjust the composition to meet the chemistry for the final applications of the steel. This invention is aimed at decreasing the loss of additives during the injection in the steel bath and thereby reducing the consumption.

**BACKGROUND INFORMATION**

Steel making is essentially an oxidation process where the impurities (i.e. the undesirable elements) of the molten metal (either pig iron or melted scrap) are preferentially oxidized to join the slag along with fluxes. Some amount of oxygen and the inclusions, like alumina formed due to subsequent de-oxidation process, remain in the steel. These oxygen and inclusions not only create operational problems during further processing of the steel in continuous casting and rolling but also are mostly detrimental to the product quality. The major challenge to the steel plant operators is to reduce their content below a certain level.

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The use of calcium is beneficial in this direction. However, the introduction of it in liquid steel bath is very difficult due to its low density and high vapour pressure. The advent of cored wire injection technology and the development of calcium bearing material like calcium-silicide, calcium-iron etc. have enabled the steel plant operators to introduce the calcium in steel baths.

A large number of steel plants have also started using cored wire with Lead, Sulphur, Selenium, Tellurium and Bismuth as filing materials. A cored wire is a continuous steel tube filled with either a calcium bearing material or a ferroalloy material. This wire is fed in the liquid steel bath contained in a ladle with the help of a wire feeder. This appears to be the most suitable means to introduce a particular element into the melt while attaining a high degree of homogenization and ensuring its metallurgical effectiveness. There exists equipment today that is capable of feeding wire at very controlled rates into the steel-melts.

The distribution of the amount of calcium injected can be in undesirable reactions like some amount being vapourised and lost to the atmosphere in unreacted condition and some amount of calcium reacting with ladle top also lost.

Some amount of calcium will react with the dissolved oxygen and inclusions present in the steel and join the slag. Some amount of calcium will remain in the steel as retained calcium. The last mentioned reactions are desirable reactions.

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Ideally the injected calcium should be involved in the desirable reactions only. The yield of calcium can be defined as the ratio of amount of retained calcium to the amount of calcium injected.

The yield of calcium in the cored wire injection process is at the most 30% and sometimes it becomes as low as 2% depending on grades of steel processed and the operating conditions.

When the steel plants are desperately looking for cost reduction options, there exists a need for an improvement in the yield of calcium. An increase of 10% in the yield of calcium should lead to big savings.

The description for addition of calcium given above holds good for other alloying additives also.

### **SUMMARY OF THE INVENTION**

The main object of the present invention therefore, is to decrease the loss of additives during the injection in the steel bath and thereby to reduce the consumption.

This object of the present invention is achieved by ensuring that the additives from the cored wire are released at an appropriate place in the ladle and selecting a suitable speed of injection and appropriate dimensions of the cored wire.



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It has been observed that the utilization of calcium and other additives is maximum when material is released from cored wire very close to the bottom of the ladle so that the losses through the undesirable reactions mentioned above can be kept to a minimum. The material is released as and when the sheath melts completely. The key factors which determine the point of release of the material are the speed of injection and the dimensions of the cored wire keeping the grade of steel processed, treatment temperature, liquid column or ladle height and the material and sheath properties constant.

The diameter of the cored wire and the thickness of the mild steel casing or sheath are selected along with a suitable speed of injection to ensure that the material is released very close to the bottom of the ladle.

The diameter of wire in, for example, a 140 ton ladle having 3 meter bath depth can be selected from 13 mm to 18 mm and the sheath thickness from 0.4 mm to 0.8 mm. The exact combination of the diameter, sheath thickness and the speed will depend on the grade of steel processed, the treatment temperature and the ladle size or liquid column height in the ladle.

Thus the present invention provides a cored wire injection process for introducing fluxes and alloying additives in liquid steel bath, a cored wire injection process for introducing fluxes and alloying additives in liquid steel bath after adjusting bath temperature and the chemistry of liquid steel in a secondary treatment unit according to requirements; characterized in that said additives are released close to the bottom of the ladle by injecting at a predetermined speed a prefabricated cored wire of appropriate dimensions, depending on the grade of liquid steel, treatment temperature and ladle size / liquid column height.

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The invention will now be described with the help of the accompanying drawings.

**BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS**

- Figure 1 shows in schematic form the use of cored wire in steel bath.
- Figure 2(a) shows the travelled distance before melting of 13 mm wire with 0.4 mm sheath thickness.
- Figure 2(b) shows variation of travelled distance with different wire dimensions.
- Figure 3 shows an improvement in the yield of material;
- Figure 4 shows the reduction in consumption of calcium material.

**DETAILED DESCRIPTION OF THE INVENTION**

The process of injecting flux and other alloying additives by means of a cored wire has been illustrated schematically in Figure 1.

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After the steel is made in the primary steel-making vessel, the liquid steel is carried in a ladle to the secondary treatment unit. The main purpose of the secondary treatment unit is to further refine the steel, adjust the bath temperature and chemistry to suit the demand of the next processing unit i.e. casting unit. The presence of dissolved oxygen and inclusions in the liquid steel poses problem to the smooth operation of casting and also deteriorate the product quality. The calcium treatment of the steel, thus, becomes essential to control the dissolved oxygen level as well as the shape and characteristics of the inclusions. The liquid steel is treated with the calcium and / or other additives bearing cored wires in the secondary processing units.

The present invention shows that the variety of steel grades a steel shop produces, requires varying specification of the cored wire to exploit maximum benefit from it. It has been already established that, if the additives are released at the maximum possible depth of the bath (i.e. close to the ladle bottom), the maximum benefit can be obtained.

In the present invention an elaborate mathematical model has been developed to predict distance travelled by a cored wire before complete melting of the sheath and thereby releasing the filling material when injected in a molten bath. Based on the model results and the experimental results discussed later in the "experimental work" section, it is clear that the most common cored wires of 13 mm diameter with 0.4 mm sheath thickness is not suitable for steel grades having high liquidus temperature and / or high treatment temperature in 140 ton capacity ladle with around 3 meter bath depth. The best wire for such applications should have 18 mm diameter and 0.8 mm sheath thickness and the injection speed should be in the range of 110-120 m / min.

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The parameters of the wire which effect the distance travelled are discussed below. The distance travelled is the distance travelled by the wire before the additive material is set free into the melt and is an indicator of the point of release of the material in the ladle.

The melting of wire and subsequent release of the material depends on the amount of heat transferred from the bath to the wire which in turn depends on the heat transfer coefficient only when the superheat and wire diameter are fixed. The heat transfer coefficient is directly proportional to the wire speed. Thus, the speed of injection decides the melting behavior when all other parameters are constant; for example higher speed results in a lower melting time.

Figure 2(a) shows the variation of distance travelled for a typical wire specification. It is observed that the distance travelled by the wire does not monotonically increase with the increase in speed; rather it passes through a maximum and beyond a critical speed it decreases again. As it is already discussed the melting time decreases with the increase in speed. However, the decrease in the melting time on account of this factor is not necessarily accompanied by a decrease in the distance travelled. On the contrary, as evident from the Figure 2(a), the distance travelled, initially increases with speed (up to line AA') and reaches a maximum at a certain speed (speed at the intersection with line AA'') and then decreases (after line AA'). The position of this intersection point changes with the treatment temperature.

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The change in the distance travelled by the wire with increase in the speed of injection is dependent on the relative dominance of the two competing factors. The increase in speed clearly implies that if the melting time were to remain unchanged, the distance travelled would be more. However, since the heat transfer coefficient also increases with the speed the melting time decreases. Clearly, whether the injected wire will move deeper or not would be dictated by whether the decrease in melting time is significantly higher or not. In the region of speed lower than the value indicated by the line AA', the first factor dominates and thus, the distance travelled increases with the speed. After this point, the dominance of the second factor prevails and so as the speed increases the distance travelled decreases in this region. It suggests that depending on the prevailing conditions in a steel shop, an increase in speed may not necessarily help the wire to travel nearer to the bottom of the ladle before release of the material.

The second rise in the curves of distance travelled after AA' is not of practical interest because of the unrealistic speed and / or very high treatment temperatures. However, this phenomena occurs as there is a minimum time required for the casing or sheath to heat up to its melting point to initiate melting. The wire, travelling at a very high speed, travels to a higher distance by this time and thus, the distance travelled by the wire increases at a very high speed.

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The problem of early release of material may result in higher evaporation loss as well as loss of unreacted material by the reaction with the top slag. The possibilities of increasing distance travelled by the wire in such situations by modifying wire dimensions have been assessed in this section. Now, if the wire diameter is increased, the total heat requirement for melting of the wire increases as there is more wire mass to be melted and as a result the release of the material is delayed. Similarly, if the casing thickness is increased, the heat requirement for its melting increases which again results into the delayed melting of the wire.

To find out the suitable dimensions of the wire for certain critical applications, the study was carried out for three wire diameters (13, 16 and 18 mm) and three casing thickness (0.4, 0.6 and 0.8 mm) and the results have been plotted in Figure 2(b). The process parameters for a typical low carbon heat (liquidus of bath as 1525°C and bath temperature at the time of injection as 1630°C are considered for this figure). Three curves for 0.4 mm casing thickness, if compared, clearly shows the consistent increase in distance travelled when the diameter is increased from 13 mm (dashed line 'c') to 16 mm (dashed line 'b') and then to 18 mm (dashed line 'a'). Similarly observation can be made when the three curves for 0.6 mm casing thickness of different wire diameter (solid lines 'a', 'b' and 'c') are compared.

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To estimate the effect of casing thickness alone, the set of three curves for 13 mm wire diameter with three different casing thickness viz. 0.4 mm (dashed line 'c'), 0.6 mm (solid line 'c') and 0.8 mm (solid line 'd') are compared. It is evident from this figure that effect of casing thickness is more prominent than that of wire diameter. For example, while the increase in diameter from 13 mm (dashed line 'c') to 18 mm (dashed line 'a') keeping the casing thickness fixed at 0.4 mm has a negligible effect on the distance travelled (at the injection speed of 200 m/min), the increase in casing thickness from 0.4 mm (dashed line 'c') to 0.8 mm (line 'd') for the wire diameter of 13 mm increases the distance travelled by around 0.8 m (at the injection speed of 200 m/min).

However, from practical point of view casing thickness can not be increased too high. Also there may be a limitation on the injection speed; injection speed may not be lowered below 110 m/min. Considering the above practical aspects, there should be a judicial choice of wire diameter, casing thickness and the speed of injection to enable the wire melting near the bottom of the ladle. For example, Figure 2(b) suggests that the 13 mm wire with 0.8 mm casing is more suitable than the 13 mm wire with 0.4 mm casing in case of high superheat melts as the former reaches closer to the ladle bottom before releasing the material. However, the speed of injection required ( $< 100$  m/min) to enable this wire (13 mm diameter with 0.8 casing) to reach the bottom of the ladle may be somewhat impractical from the operational point of view. The more workable solution, in such cases, would be to increase the wire diameter too along with the increase in casing thickness. Curve 'e' presents such solution; the 18 mm diameter wire with 0.8 mm casing thickness, in this case, can reach the bottom of the ladle at a reasonable injection speed of 110 m/min.

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**EXPERIMENTAL WORK**

Trials have been conducted in a steel plant results of which have been shown in Figures 3 and 4. The wire used was the conventional calcium-iron material bearing wire of 13 mm diameter with 0.4 mm sheath thickness and the injection was done at a steel bath temperature of 1630° C when the liquidus of bath was 1525° C. The reduction of injection speed (V) from 240 m/min to 150 m/min has shown an improvement in the yield of calcium as shown in Figure 3.

The next phase of trial was conducted using 16 mm calcium iron material bearing wire having 0.4 mm sheath thickness. The further improvement in the yield is evident from the Figure 3. The reduction in powder consumption to achieve the same level of treatment efficiency is shown in Figure 4.



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**WHAT IS CLAIMED IS:**

1. A cored wire injection process for introducing fluxes and alloying additives in liquid steel bath after adjusting bath temperature and the chemistry of liquid steel in a secondary treatment unit according to requirements; characterized in that said additives are released close to the bottom of the ladle by injecting at a predetermined speed a prefabricated cored wire of appropriate dimensions, depending on the grade of liquid steel, treatment temperature and ladle size / liquid column height.
2. The process as claimed in claim 1, wherein said predetermined speed of injection is preferably 110 m / min.
3. The process as claimed in claim 1, wherein dimension of said cored wire are preferably more than 13 mm in diameter and more than 0.4 mm in sheath thickness to suit steel grades of high liquidus temperature and / or treatment temperature in a 140 ton ladle with 3 m liquid column height.
4. The process as claimed in claim 3, wherein the dimensions of said cored wire are 16 mm in diameter and 0.6 mm in sheath thickness and the speed of injection is 60-80 m / min.

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5. The process as claimed in claim 3, wherein the dimensions of said cored wire are 18 mm in diameter and 0.8 mm in sheath thickness and the speed of injection is 100 – 120 m / min.
6. The process as claimed in claim 1, wherein said additive is a ferro-alloy material.
7. The process as claimed in claim 1, wherein said additive is a calcium bearing material.
8. The process as claimed in claim 7, wherein said calcium bearing material comprises calcium-silicide.
9. The process as claimed in claim 7, wherein said calcium bearing material comprises calcium iron.